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(54) Reinforced polymer composite

(57) A composite article formed by consolidation under heat and pressure of a fabric comprising (a) fusible fabric members at least partly composed of polyaryletherketone material and (b) substantially infusible reinforcing fabric members. Curved composite articles of this kind can be fabricated using the draping ability of the fabric to conform to a suitably curved consolidation mold.

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SPECIFICATION

Reinforced polymer composite

- 5 This invention relates to reinforced polymer composites and methods of making the same. 5
- It is known to make composites by moulding a fabric of reinforcing glass fibre yarns coated with a polymer applied to the yarns from a solution in a suitable solvent. However, this method is difficult to use with the advanced engineering polymers known as polyaryletherketones, since the few available solvents for these polymers tend to be expensive and unpleasant to use. Alternative methods which avoid the use of solvents by stacking and heat bonding alternate layers of the reinforcing fabric and a film of the desired polymer are also difficult to use with the polyaryletherketones, since these polymers tend not to consolidate sufficiently uniformly with the reinforcing fibres. 10
- The present invention provides composite articles and methods of making them to take advantage of the outstanding structural and other properties of the polyaryletherketones while avoiding or alleviating the aforementioned difficulties. 15
- The invention accordingly provides a composite article formed by consolidation under heat and pressure of a fabric comprising (a) fusible fabric members at least partly composed of polyaryletherketone material, preferably of diameter less than 150 micrometres, and (b) substantially infusible reinforcing fabric members. 20
- The incorporation, according to this invention, of the polyaryletherketone in the form of fabric members (preferably of less than 150 micrometres diameter) into a fabric together with the reinforcing fabric members improves the uniformity of consolidation, and takes advantage of the desirable draping and "give" characteristics of a fabric to conform more easily and more accurately to a required complex curvature, especially aspherical, domed, or hemispheroidal, or paraboloid, preferably hollow, curvature, when a curved composite article e.g. a sheet or panel is required. There is accordingly less risk of the irregularities due to wrinkling, which can occur when polymer films are used, and the fabric may advantageously be fashioned with a required curvature during its fabrication. The polyaryletherketone fabric members may themselves incorporate reinforcing monofilaments, provided that the diameter does not become too large or the stiffness too great, for successful fabrication of composites having paraboloid or spheroid profiles (i.e. curved domes, panels or shells) which are desired for some end uses. Fabric members of polyaryletherketones without such reinforcement are preferred for weaving or knitting fabrics in such profiles. 25
- The fusible fabric members are preferably filaments or fibres of the polyaryletherketone material of diameter less than 125 micrometres, more preferably less than 100 micrometres, and most preferably 75 micrometres or less. 30
- The consolidation of the fabric to form the composite article either alone, or with layers of other materials, or with further layers of the same fabric superposed on each other, may be effected by any appropriate application of heat and pressure. It is convenient to effect the consolidation during moulding to form a curved article. References to "fusible" and "substantially infusible" fabric members will be understood in terms of fusibility or substantial lack of fusibility under the conditions used to effect the consolidation of the fabric. 35
- The fabric may be in any convenient form, for example woven, non-woven, knitted, or braided, and comprise long monofilaments, chopped monofilaments, staple fibres, yarns made of such filaments or spun fibres, "tows", or filament-wound fibres. Preferably, the fusible fabric members are filaments substantially entirely composed of polyaryletherketone material, preferably arranged in multi-filament yarns. The configuration or arrangement of the fibres, filaments etc., in the fabric is not critical, provided that the desired distribution of the materials and uniformity of consolidation are achieved. Woven fabrics are preferred. 40
- The polyaryletherketones are aromatic polymers, by which is meant polymers which have arylene units incorporated in the repeating unit of their backbone chain, not merely appended as side groups to the chain as for example in the case of polystyrene. Preferably the aromatic polymer will have no two adjacent aliphatic carbon atoms in its backbone chain and preferably will be substantially free from aliphatic unsaturation. various linkages are not intended to imply any particular regularity or pattern of interspersions, and do not exclude the presence of linkages other than those specifically stated to be present. 45
- Polyaryletherketones may be described as linear, thermoplastic polymers having the repeat unit of the formula 50
- 55
$$-X-Ar-Y-Ar'-$$
- wherein Ar and Ar' are divalent aromatic moieties bonded to X and Y through aromatic carbon atoms and wherein either one of X and Y is carbonyl, and the other of X and Y is ether. 60
- Preferably Ar and Ar' are independently selected from substituted and unsubstituted phenylene and substituted and unsubstituted polynuclear aromatic moieties. The term "polynuclear aromatic moieties" is used to mean aromatic moieties containing at least two aromatic rings, which can be fed or joined by a direct bond or a linking group. Such linking groups include, for example, carbonyl, ether, sulphone, thioether, amide, imide, phenoxy, azo, alkylene, perfluoroalkylene, carbonate, and the like. 65
- The polyarylene polyethers may be prepared by methods well known in the art, for instance the 65

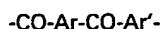
substantially equimolar one-step reaction of a double alkali metal salt of dihydric phenol with a dihalobenzenoid compound in the presence of specific liquid organic sulfoxide or sulphone solvents under substantially anhydrous conditions. Catalysts are not necessary for this reaction.

The polymers may also be prepared in a two-step process in which a dihydric phenol is first converted in situ in the primary reaction solvent to the alkali metal salt by the reaction with the alkali metal hydride, alkali metal hydroxide, alkali metal alkoxide or the alkali metal alkyl compounds. Preferably, the alkali metal hydroxide is employed. After removing the water which is present or formed, in order to secure substantially anhydrous conditions, the dialkali metal salt of the dihydric phenol is admixed and reacted with about stoichiometric quantities of the dihalobenzenoid or dinitrobenzenoid compound.

The polymerization reaction proceeds in the liquid phase of a sulfoxide or sulphone organic solvent at elevated temperatures.

The term "aromatic ether ketone polymer" or "polyaryletherketone" is used herein to include polymers containing arylene, ether and ketone linkages in the polymer chain. Other linking groups such as sulphone, thioether, amide, imide, azo, alkylene, perfluoroalkylene, carbonate or the like may also be present.

The polyaryletherketones may be better defined as polymers having the repeat unit of the formula



wherein Ar and Ar' are aromatic moieties at least one of which contains a diaryl ether linkage forming part of the polymer backbone and wherein both Ar and Ar' are covalently linked to the carbonyl groups through aromatic carbon atoms.

Preferably, Ar and Ar' are independently selected from substituted and unsubstituted phenylene and substituted and unsubstituted polynuclear aromatic moieties. The term polynuclear aromatic moieties is as hereinbefore defined.

The phenylene and polynuclear aromatic moieties can contain substituents on the aromatic rings. These substituents should not inhibit or otherwise interfere with the polymerization reaction to any significant extent. Such substituents include, for example, phenyl, halogen, nitro, cyano, alkyl, 2-alkynyl and the like.

Poly(aryl ether ketones) having the following repeat units (the simplest repeat unit being designated for a given polymer) are preferred, "Ph" representing a p-phenylene moiety:

- (I) -Ph-O-Ph-CO-
- (II) -Ph-O-Ph-O-Ph-CO-Ph-CO-
- (III) -Ph-O-Ph-CO-Ph-O-Ph-CO-Ph-CO-
- (IV) -Ph-O-Ph-O-Ph-CO-Ph-O-Ph-CO-
- (V) -Ph-O-Ph-O-Ph-CO-
- (VI) -Ph-O-Ph-CO-Ph-CO-

The polymers having repeat units (I), (II), (III) and (IV) above are especially preferred where high temperature performance and raindrop impact erosion resistance are desired. Polyaryletherketones of inherent viscosity at least 0.8, preferably at least 1.0, are advantageous.

Poly(aryl ether ketones) can be prepared by known methods of synthesis. Preferred poly(aryl ether ketones), which are advantageous for forming the fabrics used in this invention, can be prepared by a special Friedel-Crafts polymerization as described in our published European Patent application No. 124276.

In this process, a single monomer system comprising an aromatic acid halide having an acid halide group and an aromatic hydrogen atom activated toward electrophilic attack or a two-monomer system comprising an aromatic diacid dihalide and an aromatic compound having two aromatic hydrogen atoms activated to electrophilic attack is polymerized in a reaction medium comprising a Lewis acid, optionally a controlling agent such as a Lewis base, and optionally a diluent. Preferably, a Lewis base is present in the reaction medium, in which case, the amount of Lewis acid employed should be in excess of that required to complex with the Lewis base and all other basic species in the reaction mixture. If a Lewis base is not present, the amount of Lewis acid used depends on the nature of the particular monomer system used. If the monomer system contains deactivated aryloxy groups then a substantial excess of Lewis acid over that required to complex with the basic species present should be used. If the monomer system contains undeactivated aryloxy groups, only a slight excess of Lewis acid over that required to complex with the basic species present should be used. Further, if no Lewis base is used, a diluent should be present in the reaction mixture and the concentration of the monomer(s) should be above a certain level. The process provides high molecular weight, melt processable poly(arylene ether ketones) with little, if any, undesired substitution along the polymer backbone. This absence of undesired substitution makes the polymers especially suitable for making low diameter fibres for use in the fabrics of the present invention. Polyaryletherketones having less than 0.1%, preferably less than 0.01%, ortho-branching of the p-phenylene chain units are preferred, substantially gel-free, melt-stable polyaryletherketone being most suitable.

The use of thermoplastic polymer rather than thermosetting polymer is preferred for many applications for a variety of reasons. In particular thermoplastic polymer based composites may be postformed, that is once consolidated they may be reheated above the melting temperature of the thermoplastic and deformed to change the shape of the composite. This allows the composites to be made in shapes that are easy to manufacture and/or store and/or transport, the shapes being postformed later to the shape required for operation. For example thermoplastic composites may be made as flat plates and postformed into curved

plates as may be required, for example, for body sheets or panels for vehicles or aircraft. Also thermoplastics may be used which have high tensile and bending strength, high toughness, rain erosion resistance and abrasion resistance. Furthermore thermoplastic materials are typically easier to handle and fabricate into composite structures than thermosetting materials since at manufacturing temperatures the surface of some thermosetting materials tends to be "tacky", while that of a thermoplastic material is "dry".

The polyaryletherketone material may incorporate a permittivity-adjusting material, preferably a filler, for example titanium dioxide, of such permittivity and in such amount as to render the permittivity of the polyaryletherketone material closer to that of the reinforcing fabric members. The reinforcing fabric members may be provided as single fibres, or in bundles of fibres commonly known as "tows". As other examples the reinforcement may be provided by short lengths of fibres, for example as short chopped fibres or staple fibres, or by filament wound fibres. Preferably, the reinforcing fabric members will have a diameter of less than 150 micrometres, preferably less than 100 micrometres, more preferably 75 micrometres or less. Filaments of glass having a diameter of about 9 micrometres, e.g. 7-11 micrometres, are preferred, preferably incorporated in multi-filament yarns. It is preferred that the diameter of the polyaryletherketone fibres be no more than 10 times the diameter of the reinforcing members.

References to "diameter" are not to be taken as limiting the fabric members to circular cross-section, the average diameter of oval, square, or other profiles being readily determinable.

The material of the reinforcing fabric members is preferably compatible with the polyaryletherketone material, and the reinforcement is preferably incorporated in the polymeric material at a sufficiently high density to provide structural strength to the composite. As examples of fibres that may be used there may be mentioned carbon, glass, boron, alumina, silicon carbide, and silica fibre, natural fibres such as cotton, organic fibres such as nylon polyesters and polyamides, and metallic fibres such as stainless steel and aluminium. A single type of fibre may be used or a combination of different types of fibre. Also where a fibre comprises a bundle of filaments in a so-called 'tow' or 'roving' the filaments in each tow or roving may be the same or different. Thus for example a mixed tow may comprise a bundle of both organic and inorganic filaments. As examples, in some embodiments, it is preferred for at least some of the fibres to be metal, for example where the composite is to be used for electromagnetic shielding. In other embodiments it is preferred to use electrically non-conductive fibres, for example glass fibres, to prepare composites having a relatively high degree of "transparency" to electromagnetic radiation. Such composites may be used to provide radomes (radar antenna housings) for supersonic aircraft or missiles.

The softening temperature of the reinforcement fibres is preferably greater than the softening temperature of the polyaryletherketone material, preferably at least 50°C greater, although some softening of the "infusible" reinforcement during consolidation may be permissible, provided that adequate strength is retained.

The reinforcement and the polyaryletherketone material may be provided in a variety of substantially unconsolidated arrangements, by which is meant that the individual reinforcing members, or possibly cohesive groups of the same (especially yarns or tows), are not adhered together by the polyaryletherketone to any significant extent. Consolidation causes the polyaryletherketone material to spread out and join the reinforcing members (or groups thereof) together.

The invention also provides a method of making a composite article as hereinbefore described comprising providing one or more layers of the said fabric and applying heat and pressure to consolidate the fabric layer(s). Preferably the composite is shaped during the consolidation to provide a sheet or panel of complex curvature.

Appropriate heat and pressure for the consolidation of the fabric to form the composite can readily be determined by simple trial and error, pressures of 1 to 10 MN/m² at 370-420°C being suitable for shaping and consolidating an arrangement of 1 to 20 layers of the fabric using glass fibres with the polyaryletherketone of formula (I) hereinbefore listed. Preferably the glass fibres will have a size coating which is compatible with the polyaryletherketone and capable of withstanding the consolidation temperatures, but the size may alternatively be removed from the glass fibres in the fabric before consolidation.

Specific examples of the invention will now be described by way of further illustration, using polyaryletherketone having the repeat unit (I) hereinbefore listed, identified in these examples as PEK.

Example 1

A cloth was made from PEK fibre (22 filament 107 Tex twisted yarn) and glass fibre (Vetrotex EC9682X2 AS21P S80). The weave construction was an 8-end sateen, warp PEK 48 end/inch, weft glass 30 end/inch. The size was then removed from the glass by immersion for 45 minutes in 1% enzyme and detergent aqueous solution at 50°C, followed by rinsing and drying.

A cloth of PEK alone was also made, a 3/1 broken twill, warp 48 end/inch, weft 28 end/inch.

A sandwich construction of 2 layers of PEK cloth, 4 layers of PEK/glass cloth, and 2 more layers of PEK cloth, laid up in an alternating 0°, 90° fashion, each cloth being 16 cm square, was consolidated between aluminium release foils in a curved steel mould at 400°C under a force of 10 tons. This pressure was applied for 15 mins once the sandwich had reached 400°C. After cooling to room temperature under pressure, the composite was removed from the press and the aluminium foil peeled off.

The product was a composite of complex curvature and of thickness 1.5 mm containing well wetted-out glass fibres and having smooth fibre-free surfaces (due to the two surface layers of glass-free PEK cloth).

Example 2

A cloth was made from a twisted pair of PEK fibre (22 filament 107 Text twisted yarn) and glass fibre (Owens Corning EC 9-136 S40 636). The weave construction was a double equal twill with a warp and a weft density of 5 40 end/inch.

The size on the glass fibre was removed by immersing the cloth in a solution of 0.2% Teepol detergent plus 0.8% Protease B500 enzyme in water at 50°C for 45 minutes, followed by rinsing in hot and cold water.

A sandwich construction of 6 layers of cloth, laid up in an alternating 0°, 90° fashion, each cloth being 16cm square, was consolidated between aluminium release foil in a curved steel mould at 400°C under a force of 10 10 tons. This pressure was applied for 15 mins once the sandwich had reached 400°C. After cooling to room temperature under pressure the composite was removed from the press and the aluminium foil peeled off.

The product was a composite of complex curvature and of thickness 3.30mm containing well wetted-out glass fibre firmly bonded to the PEK.

15 CLAIMS

1. A composite article formed by consolidation under heat and pressure of a fabric comprising (a) fusible fabric members at least partly composed of polyaryletherketone material and (b) substantially infusible reinforcing fabric members.
- 20 2. An article according to claim 1, wherein the fusible fabric members initially were less than 150 micrometers in diameter.
3. An article according to claim 1 or 2 wherein the consolidated fabric occupies a curved configuration of complex curvature.
4. An article according to claim 3 having a domed, paraboloid, or spheroid hollow curvature.
- 25 5. An article according to any of the preceding claims, wherein the fusible fabric members are filaments of polyaryletherketone material, preferably incorporated in multi-filament yarns.
6. An article according to any of the preceding claims, wherein the polyaryletherketone material has an inherent viscosity of at least 0.8 preferably at least 1.0.
7. An article according to any of the preceding claims, wherein the fusible fabric members initially were 30 less than 100 micrometers, more preferably 75 micrometres or less, in diameter.
8. An article according to any of the preceding claims, wherein the reinforcing fabric members have a diameter of less than 150 micrometres, preferably less than 100 micrometres, more preferably 75 micrometres or less.
9. An article according to claim 8, wherein the reinforcing fabric members are filaments of glass having a 35 diameter of about 9 micrometres, preferably incorporated in multi-filament yarns.
10. An article according to any of the preceding claims, wherein the diameter of the fusible fabric members initially was not more than 10 times the diameter of the reinforcing members.
11. An article according to any of the preceding claims, wherein the consolidated polyaryletherketone material incorporates a permittivity-adjusting material, preferably a filler, for example titanium dioxide, of 40 such permittivity and in such amount as to render the permittivity of the polyaryletherketone material closer to that of the reinforcing fabric members.
12. An article according to any of the preceding claims, wherein the polyaryletherketone material comprises a polymer of repeat unit
-Ph-O-Ph-CO-
45 or
-Ph-O-Ph-CO-Ph-O-Ph-CO-Ph-CO-
or
-Ph-O-Ph-O-Ph-CO-Ph-O-Ph-CO-
or
50 -Ph-O-Ph-O-Ph-CO-Ph-CO-
wherein Ph represents a p-phenylene moiety.
13. A method of making a composite article according to any of the preceding claims comprising providing one or more layers of the said fabric and applying heat and pressure to consolidate the fabric layer(s).
- 55 14. A method according to claim 13, wherein the article is shaped during the consolidation to provide a sheet or panel of complex curvature.